Absence of commensurate ordering at the polarization flop transition in multiferroic $DyMnO_3$

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Ferroelectric spiral magnets $DyMnO_3$ and $TbMnO_3$ show similar behavior of electric polarization in applied magnetic fields. Studies of the field dependence of lattice modulations on the contrary show a completely different picture. Whereas in $TbMnO_3$ the polarization flop from $P\|c$ to $P\|a$ is accompanied by a sudden change from incommensurate to commensurate wave vector modulation, in $DyMnO_3$ the wave vector varies continuously through the flop transition. This smooth behavior may be related to the giant magnetocapacitive effect observed in $DyMnO_3$.

The ability to control ferroelectric polarization ($\boldsymbol{P}$) with an applied magnetic field ($\boldsymbol{H}$) in manganite perovskites and related materials has caused a resurgence of interest in magneto-electric phenomena. One of the most striking effects is the five-fold increase of the dielectric constant of $DyMnO_3$ in magnetic field, named giant magnetocapacitance.[1] The key to this unprecedented sensitivity is the spiral magnetic ordering stabilized by competing exchange interactions, which forces positive and negative ions to shift in opposite directions and which can be rather easily influenced by applied magnetic fields.

Unlike conventional ferroelectrics, in the $R\mathrm{MnO_3}$ manganite perovskites such as R=Tb and Dy the emergence of ferroelectricity[2,3] arises from the peculiar coupling of the lattice to a spiral ordering of Mn-spins.[4,5,6] Spiral ordering is defined by the wave vector $\boldsymbol{\kappa}$ and the axis $\boldsymbol{e}$ around which the spins rotate. For R=Tb and Dy these two vectors are perpendicular to each other.[4] The coupling of a uniform electric polarization $\boldsymbol{P}$ to an inhomogeneous magnetization $\boldsymbol{M}$ is phenomenologically described by a term linear in the gradient $\boldsymbol{\nabla M}$, the so-called Lifshitz invariant. Such a coupling breaks the inversion symmetry of the crystal lattice in the spiral magnetic state and induces the direction of the polarization $\boldsymbol{P}= \gamma\chi M_1 M_2[\boldsymbol{e}\times\boldsymbol{\kappa}]$, where γ and χ are a coupling constant and the dielectric susceptibility, M_1 and M_2 are amplitudes of the magnetic moments in directions perpendicular to $\boldsymbol{e}$.[6] For R =Tb and Dy, $\boldsymbol{\kappa}$ is parallel to the b-axis and $\boldsymbol{e}$ parallel to the a-axis, so that the ferroelectric polarization induced below the spiral ordering temperature T_C, is parallel to the c-axis ($P\|c$).[2]

The application of magnetic field either parallel to the a- ($H\|a$) or b-axis ($H\|b$) leads to a flop of the polarization from $P\|c$ to $P\|a$. The flop in the polarization is interpreted as the flop of the vector $\boldsymbol{e}$ from the a- (spins within the bc-plane) to the c-direction (spins within the ab-plane). For R=Tb these field-induced flops of $\boldsymbol{P}$ occur at critical field of H_C^a∼8 T and H_C^b∼4.5 T at 4 K for field parallel to the a- and b-axis respectively and are associated with a first order transition from an incommensurate (IC) low field magnetic ordering to a commensurate (CM) high field phase. The H-T-phase diagram of $DyMnO_3$ is very similar to the one of $TbMnO_3$, with the same characteristic flops of $\boldsymbol{P}$ but at lower critical fields, H_C^a∼6.5 T and H_C^b∼1 T at 2 K.[3]

In this paper we show, that although the phase diagrams of R=Dy and Tb may be qualitatively similar, their structural behavior at H_C is completely different. We find that for $DyMnO_3$ the polarization flop is not associated with a transition to a CM phase as in the case of R =Tb, but rather the magnitude of the wave vector changes very little across H_C for both $H\|a$ and $H\|b$ configurations. We argue that the magnitude of the incommensurability for R=Dy does not lie sufficiently close to a CM value, as opposed to R=Tb, making the IC high field phase energetically more favorable.

For R=Dy, Mn-spins order to form a longitudinal spin density wave (SDW) below T_N∼39 K with wave vector $\boldsymbol{\kappa} = \delta_m \boldsymbol{b^*}$ with $\delta_m^{Mn}\sim$ 0.36...0.385[3] determined on the basis of lattice reflections with δ_l=2δ_m[3,7,8] that arise from a coupling of the IC magnetic ordering to the lattice via a quadratic magneto-elastic coupling.[9] With further cooling δ_m^{Mn} decreases down to T_C=19 K, where a second transition into the spiral phase occurs. Coincident with the transition to a spiral phase a spontaneous electric polarization parallel to the c-axis is found.[2] Below T_N^{Dy}=5 K Dy magnetic moments order commensurately with propagation vector $\frac{1}{2}\,\boldsymbol{b^*}$.[8] In the study presented here, structural first and second harmonic reflections related to the magnetic first harmonic reflections are investigated.

Single crystalline samples were prepared using the floating zone technique at the HMI. Details of sample preparation and characterization are given elsewhere.[8] Due to the high neutron absorption cross section of Dy, in-field neutron diffraction is not ideal to investigate field induced magneto-structural transitions in $DyMnO_3$. Rather to investigate the structural response to the field

induced polarization flop we have utilized in-field synchrotron x-ray diffraction with the two field configurations $H\|a$ and $H\|b$. Measurements with $H\|a$ were performed at beamline X21 at the National Synchrotron Light Source at Brookhaven National Laboratory with a photon energy of 9.5 keV, using a 13 T Oxford cryomagnet with vertical field. Measurements in the $H\|b$ configuration were carried out at beamline BW5 at HASYLAB with a photon energy of 100 keV using a 10 T Cryogenics cryomagnet with horizontal field. Magnetization measurements were performed with a Physical Properties Measurement System (PPMS) on a 14.5 mg $DyMnO_3$ sample. The spontaneous electric polarization as a function of field and temperature was determined from the pyro-current recorded in a PPMS-system using an electrometer.

Measurements of the spontaneous electric polarization performed on the same samples used in our diffraction experiments in magnetic field configurations $H\|a$ and $H\|b$ (insets in Fig. 1c and Fig. 2 a) confirm that spontaneous ferroelectric polarization is present below T_C=19 K as already reported in Ref. 3. The application of $H\|b$ below $T_C(Dy)$ results in the suppression of $P\|c$ (inset of Fig. 1c). Kimura *et al.* show in addition that this decrease is accompanied by an increase in $P\|a$ indicative of the flop in the ferroelectric polarization.[3]

In Fig. 1a-b we show the temperature dependence of the wave vector and integrated intensity of the second harmonic reflection (0, 4-2δ, 0), both for decreasing and increasing temperature. The dependences are compared for zero field ($P\|c$), and $\mu_0 H\|b = 10$ T ($P\|a$). In both data sets, we find a significant hysteresis in the intensity as well as in the magnitude of δ around T_C=18 K, which is associated with the onset of ferroelectricity. However, despite the fact that $\boldsymbol{P}$ lies along different axes for 0 and 10 T, we observe no significant change between these two measurements. In Fig. 1c-d, we show the field dependence of δ and of the integrated intensity of the same reflection at T=2 K. Here we find a small initial increase of δ up to $\mu_0 H_C^b$=1 T where the flop in polarization is found while the intensity of the same reflection shows a steady increase with increasing field. Above H_C^b, we find a small decrease of δ with increasing field. This behavior is in sharp contrast to $TbMnO_3$ where δ varies slowly with increasing field and locks in above H_C^b into a CM value of $\boldsymbol{\kappa}=\frac{1}{4}\mathbf{b^*}$ at H_C^b.[10]

In Fig. 1e-f, the temperature dependence of δ and the intensities of first and second harmonic reflections is shown for data measured in field cooling with $\mu_0 H\|b =$ 2.5 T. Here we find a different behavior in the intensities of IC reflections. For wave vector along the b*-direction (0, 4-2δ, 0), a strong hysteresis is observed in its intensity as a function of temperature, whereas this hysteresis is absent for wave vectors that are mainly along the c*-direction ((0, δ, 5) and (0, 2δ, 5)) (Fig. 1f). Nevertheless, δ and its hysteresis are the same for all reflections (Fig. 1e). The described intensity behavior is similar to what we have recently observed in zero field temperature

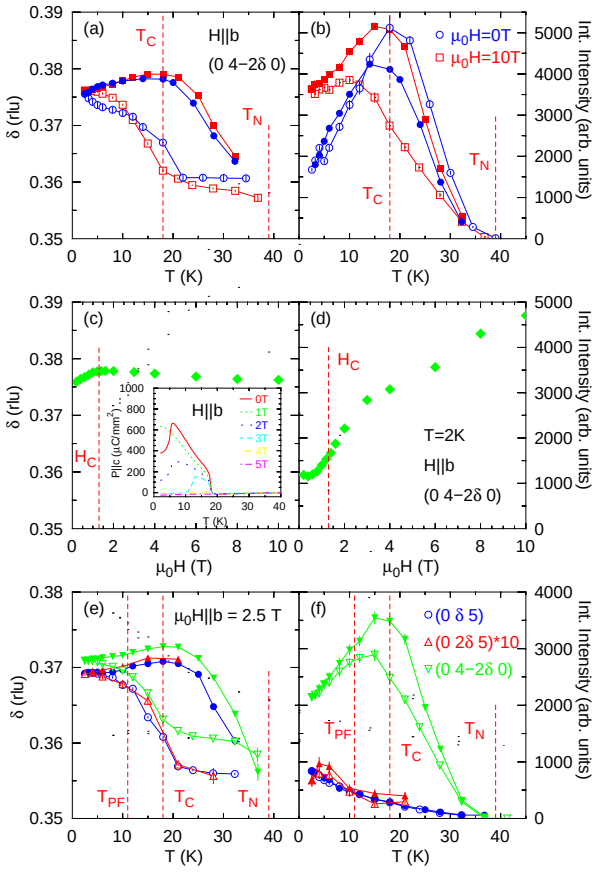

FIG. 1: (color online) Temperature dependence of (a) the incommensurability δ and (b) the respective intensities of the (0, 4-2δ, 0) structural reflection. Data are shown for $\mu_0 H = 0$ T and $\mu_0 H\|b = 10$ T for decreasing (open symbols) and increasing (closed symbols) temperature. In panel (c) and (d), δ and intensity variation as function of magnetic field, respectively, are shown for a sample temperature of $T = 2$ K, in the same axes ranges as in (a) and (b). In the inset, spontaneous electric polarization $P\|c$ is shown as function of temperature for magnetic field orientation $H\|b$. Temperature dependence of (e) wave vector and (f) the respective intensities for $\mu_0 H\|b = 2.5$ T and wave vectors (0, δ, 5), (0, 2δ, 5) and (0, 4-2δ, 0) for decreasing (open symbols) and increasing (closed symbols) temperature. The (0, 2δ, 5) intensities in (f) are multiplied by a factor of 10.

dependent measurements using resonant x-ray scattering from a single crystal of $DyMnO_3$.[11] In these measurements a similar hysteresis was observed to be associated with the induced ordering of Dy-spins with the same propagation vector as that for the Mn spin ordering. Finally for this field configuration we note that at 2.5 T, the polarization flop from $P\|a$ to $P\|c$ is expected with increasing temperature at $T_{PF} \sim 12$ K (inset in Fig. 1c). However our diffraction measurements find no anomaly either on the temperature dependence of the wave vector or in the intensities at this temperature as it was found in $TbMnO_3$.

We now turn our attention to measurements conducted

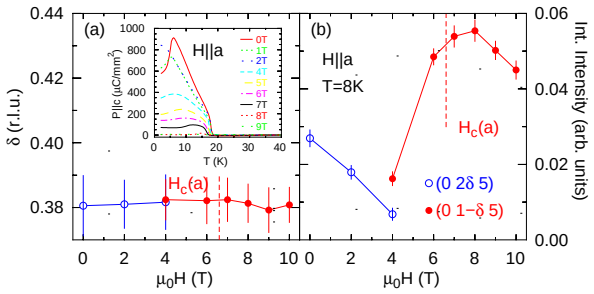

FIG. 2: (color online) Field dependences with field $H\|a$ of (a) the incommensurability and (b) the integrated intensity measured at $T = 8$ K. The error bars in (a) represent the HWHM of the superlattice reflection. In the inset, spontaneous electric polarization $P\|c$ is shown as function of temperature for magnetic field $H\|a$.

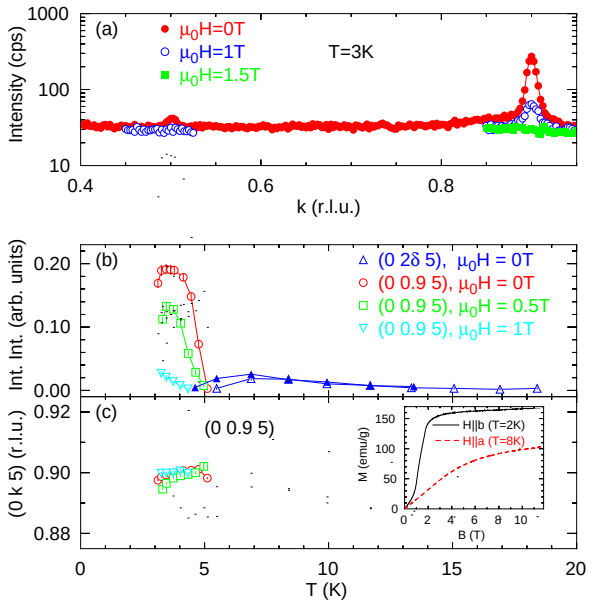

FIG. 3: (color online) (a) Scans along (0, k, 5) at $T = 3$ K for different applied magnetic fields with intensity in logarithmic scale. (b) Temperature dependence as function of field $H\|a$ of the integrated intensity of the superlattice reflections (0, 0.9, 5) in the Dy ordered phase and the second harmonic reflection (0, 2δ, 5) due to Mn order. Open and closed symbols represent increasing and decreasing temperature, respectively. In (c) the wave vector of the (0, 0.9, 5) reflection is shown as function of temperature for different fields. The inset shows magnetization data of $DyMnO_3$ for $H\|a$ and $H\|b$.

in the $H\|a$ configuration. In Fig. 2a-b the field dependence of the intensity and wave vector of the first and second harmonic reflections (0, 1-δ, 5) and (0, 2δ, 5) is shown, measured at $T = 8$ K above the ordering temperature of Dy of $T_N^{Dy} \sim 5$ K. The second harmonic reflection decreases in intensity with increasing field and vanishes at 5 T, while the first harmonic appears only at a field of 4 T and saturates in intensity at 7 T. This behavior is not directly related to the polarization flop but reflects a variation of the modulation direction of the strain wave leading to the superlattice reflections. However the most remarkable behavior is found for the field dependence of the wavevector. Here, the wave vector of the first harmonic reflection does not change significantly through the polarization flop transition at $\mu_0 H_C^a \sim 6.5$ T.[3] Again this is in sharp contrast to the behavior of $TbMnO_3$, where a discontinuous transition to a CM phase is found.

Below 6K, Dy spins order commensurately with $\delta_m^{Dy} = \frac{1}{2}$. Previously we have argued that the lattice distortion associated with this magnetic ordering is not CM but rather IC with $\delta_l \sim 0.1\mathbf{b}^*$.[8] In our measurements we found the half-integer magnetic reflection to be extremely weak and we focused our attention to the lattice $\delta_l \sim 0.1$ satellite measured at (0, 0.9, 5). In Fig. 3a we show a series of scans at different fields applied along the a-axis at 3 K which show the rapid suppression of the $\delta_l \sim 0.1$ satellite which vanishes for fields $\mu_0 H\|a > 1$ T. The CM magnetic reflection (0, 0.5, 5) is only measurable at zero field and can not longer be observed at 1 T. The temperature dependence of the intensity and wavevector of the (0, 0.9, 5) reflection is shown in Fig. 3b-c, revealing the rapid suppression of the intensity of this reflection at low temperature in accordance with the appearance of ferromagnetic order (inset Fig. 3c), indicating an easy axis along the b-direction. The suppression of this reflection with magnetic field is analogous to a similar behavior found for R =Tb which coincided with the ferromagnetic ordering of Tb-spins for the same field size and configuration.[10]

The polarization flop is driven by the field-induced flop of the axis of rotation of the magnetic spiral $\boldsymbol{e}$. Its direction is determined by magnetic anisotropy terms, which to lowest order of the free energy expansion in powers of magnetization of Mn spins have the form, $\sum_{\alpha=a,b,c} a_\alpha M_\alpha^2$. Phenomenologically the spin flop transition results from the field dependence of the coefficients a_α. Below the critical field H_C, $a_b < a_c < a_a$, which favors spins rotating in the bc plane ($e\|a$), while above H_C, $a_b < a_a < a_c$, favoring the rotation in the ab-plane ($e\|c$).

From the perspective of symmetry there is no restriction that the high field spiral phase must be CM. In this view the fact that there is a magneto-elastic phase transition to a CM phase associated with the flops in the polarization for R =Tb would appear to be a special case, especially when compared to R =Dy where we find no such transition at H_C. The difference in behavior between these two multiferroics is not of fundamental nature but rather simply lies in the magnitude of the incommensurability. For R=Tb, δ_m=0.28 r.l.u. is close to the CM value of $\frac{1}{4}$. For this CM value of the wave vector the amplitude of the Mn magnetic moment is not modulated[10] and may thus be energetically more favorable than an IC amplitude modulated phase. In the phenomenological approach the CM state with $\delta = 0.25$ r.l.u. is stabilized by M^4 terms in the Landau expansion. For R=Dy the value of δ=0.38 r.l.u. is further away from a

CM value ($\frac{1}{3}$) and thus a transition to it is not favorable energetically. Therefore the Mn spin spiral may indeed flop as expected but without a change in δ.[13] Clearly here the modulation period in real space is much shorter, and the amplitude of the Mn magnetic moment is modulated.

A significant difference between the two multiferroics is found in the behavior of the complex magnetic ordering of R-ions. For R=Tb, Tb spins are induced to order along the a-axis below T_N with the same periodicity as Mn-spins and below T_N^{Tb}=7 K they order separately with δ_m^{Tb} =0.42 r.l.u. At low temperatures, when $H\|a\sim$1 T, Tb-spins are aligned ferromagnetically, while for field along the b-axis, δ_m^{Tb} jumps discontinuously to a CM value of $\frac{1}{3}$ at 1.75 T.[10] The behavior for R=Dy is much simpler, as below T_N^{Dy}=6 K the Dy spins order with $\delta_m^{Dy} = \frac{1}{2}$. Here, the suppression of the IC-reflections together with the magnetization data indicates a melting of the antiferromagnetic Dy ordering, a behavior different to $TbMnO_3$.

On the basis of the CM ordering of Mn-spins for the $P\|a$ phase for R=Tb it has been suggested that ferroelectricity may arise in the absence of a spiral magnetic ordering. Here an exchange striction mechanism proposed from competing ferromagnetic and antiferromagnetic super-exchange interactions predicts a $P\|a$ phase for a CM ordering with $\delta = \frac{1}{4}$. This model holds strictly for a CM ordering and suggests that for R=Dy the spiral phase must be maintained at high fields to support a ferroelectric state.

The smooth magnetic field dependence of the spiral wave vector in $DyMnO_3$ at the spin flop transition may explain the large increase of the dielectric constant ε_a, observed in this material.[1,3] If higher-order terms in the Landau expansion of free energy could be neglected, then at the spin flop transition the magnetic excitation spectrum of the spiral would acquire a zero mode, since for $a_a(H_C) = a_c(H_C)$ there is a freedom to rotate the spiral plane around the b axis. This mode can be excited by electric field $E\|a$ normal to the spiral bc-plane and is the electromagnon studied in Ref. 12. Its softening at $H = H_C$ would result in divergence of static dielectric susceptibility ε_a. In reality, due to higher-order terms in the Landau expansion the spin flop transition is of first order, the softening of the magnetic mode is not complete and the peak value of the dielectric constant is finite. Still, in $DyMnO_3$ this transition is close to a second-order one in the sense that the spirals above and below the critical field are essentially the same except for their orientation. The softness of the spiral magnetic ordering at the critical field may be the reason behind the large magnetocapacitance observed in $DyMnO_3$ which becomes truly gigantic close to the tricritical point at the crossing of the collinear and two spiral phases with $P\|c$ and $P\|a$, where higher-order terms are small. In $TbMnO_3$ the spin flop transition is strongly discontinuous due to the concomitant IC-CM transition, which limits the growth of the dielectric constant.

In summary, in-field synchrotron X-ray diffraction measurements from a $DyMnO_3$ single crystal have shown that there is no change of the wave vector δ associated with the flop of the ferroelectric polarization $\mathbf{P}$ at H_C for both $H\|a$ and $H\|c$. This is in sharp contrast to similar measurements reported for $TbMnO_3$ were a transition to a CM phase is found at H_C for the same field configurations. We argue that the magnitude of the incommensurability for R =Dy does not lie sufficiently close to a CM value, as opposed to R=Tb, making the IC high field phase energetically more favorable.

Acknowledgments

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